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Two novel ultralow temperature firing microwave dielectric ceramics $LiMVO_6$ (M = Mo, W) and their chemical compatibility with metal electrodes

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ABSTRACT

Low temperature cofired ceramics technology (LTCC) has been widely studied and used in wireless communication because of their outstanding capability for device miniaturization and integration. However, many commercial microwave dielectric materials have high sintering temperatures that pose challenge for cofiring with inner electrodes. Herein, two brannerite vanadate $LiMVO_6$ (M = Mo, W) ceramics with intrinsically low sintering temperatures were prepared. Dense and stable $LiMVO_6$ (M = Mo, W) ceramics could obtained at 640 °C for $LiMoVO_6$ and 700 °C for $LiWVO_6$. Favorable microwave dielectric properties were also obtained with $\varepsilon_r = 13.3$, $Q \times f = 12{,}460$ GHz, and $\tau_f = +101.0$ ppm/°C for $LiMoVO_6$ and $\varepsilon_r = 11.5$, $Q \times f = 13{,}260$ GHz, and $\tau_f = +163.8$ ppm/°C for $LiWVO_6$. Moreover, the relationship between crystal structure and microwave dielectric properties was studied by means of packing fraction, bond valence, and octahedral distortion. Their chemical compatibility with the metal electrodes were confirmed.

1. Introduction

The rapid development of wireless telecommunication, especially the recent explosion in the uses of wireless data transfer, e.g. the Tactile Internet (5G wireless systems), Internet of Things (IoT), and satellite broadcasting, has triggered the extensive studies on the microwave dielectrics with high performance [1–5]. During recent decades, low temperature cofired ceramic (LTCC) technology, as a key approach in fabricating highly integrated devices, has attracted significant attention owing to its advantageous utilization in microelectronics, microsystems and microwave modules. In order to cofire with the inner electrode (e.g. Ag), the low sintering temperature ($T_{s<}$ 960 °C) is a critical requirement for commercial applications in LTCC [6,7].

To date, several methods have been proposed to lower the sintering temperature of dielectric ceramics. One effective approach is to add low melting point oxides or glasses, such as CuO, B_2O_3, V_2O_5, but always accompanied by degradation on microwave dielectric properties, especially the quality factor. Thus, searching for novel glass-free low temperature firing ceramics has become a hot research topic, which mainly focuses on the Li-based, V-based, W or Mo-based systems due to the low melting points of the raw constituents. For example, Li-containing compounds with rock salt structure, such as Li_2TiO_3 and Li_3NbO_4, were reported to exhibit a combination of low sintering temperature and excellent microwave dielectric properties [8–10]. Zhou et al. [11–13] reported some low-firing molybdates microwave dielectric ceramics. In our previous work, a series of V_2O_5 rich compounds were reported to possess a combination of promising microwave dielectric properties and low firing temperatures [14–16]. Therefore, it is reasonable to predict that a compound containing Li, Mo, W and V simultaneously would possess low sintering temperature and combined good dielectric properties. Thus, in this work, $LiMVO_6$ (M = Mo, W) ceramics were prepared and the structure were investigated by means of XRD, SEM, and Raman spectroscopy. Furthermore, the thermal properties and microwave dielectric properties of $LiMVO_6$ (M = Mo, W) ceramics were characterized.

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2. Experimental procedure

2.1. Sample preparation

$LiMoVO_6$ and $LiWVO_6$ compounds were individually synthesized through a conventional solid-state reaction method. Proportionate amounts of reagent-grade raw materials, Li_2CO_3 (>99%, Guo-Yao Co., Ltd., Shanghai, China), NH_4VO_3 (>99%, West Long Chemical Co., Ltd., Guangdong, China), MoO_3 and WO_3 (>99%, Guo-Yao Co., Ltd., Shanghai, China), were measured according to the general formula $LiMVO_6$ (M = Mo, W). Powders were mixed and ball-milled in alcohol medium for 6 h in nylon battle with zirconia balls. After drying at 120 °C, the $LiMoVO_6$ and $LiWVO_6$ powers were calcined at 500 °C and 600 °C for 6 h, respectively. The calcined $LiMoVO_6$ and $LiWVO_6$ powers were re-milled for 6 h individually ground and pressed into cylinders (10 mm in diameter and 6 mm in thickness) in a steel die under a pressure of 200 MPa with polyvinyl alcohol (PVA, 10 vol%) as a binder. The $LiMoVO_6$ pellets were sintered at 540–640 °C for 6 h in air and $LiWVO_6$ pellets were sintered at 620–720 °C for 6 h in air.

2.2. Characteristics

The crystalline phases of ceramics were identified by X-ray diffraction method (Cu*Kα1*, 1.54059 Å, Model X'Pert PRO, PANalytical, Almelo, Holland). The diffraction patterns were taken at room temperature in the range of 10°-80° by step scans. Raman spectras were recorded at room temperature using a DXR Raman Microscope (Thermo Fisher Scientific DXR, America). The particle morphologies of the samples were examined by scanning electron microscopy (FE-SEM, Model S4800, Hitachi, Japan). The thermal properties of $LiMVO_6$ (M = Mo, W) were examined by means of thermogravimetry (TG) and differential thermal analysis (DTA) using an analyser with the simultaneous recording of weight losses and temperature variations. The bulk densities of the ceramics were measured using the Archimedes method. The relative permittivity (ε_r) and quality factor ($Q \times f$) of the samples were measured using a network analyzer (N5230A, Agilent, America) and the temperature coefficient of resonant frequency (τ_f) was obtained by noting the temperature shifts of the resonance scope from room temperature to 85 °C using a temperature chamber (Delta 9039, Delta Design, San Diego, CA).

3. Results and discussion

3.1. Phase formation and crystal structure

TG-DTA curves of the mixed raw powders for $LiMVO_6$ (M = Mo, W) are shown in Fig. 1 to understand the chemical reaction occurring during the calcination. Both samples show similar curves. Three weight loss regions accompanied by obvious exothermic DTA peaks can be observed in the TG curves from 50 °C to 550 °C. A remarkable exothermic peak located at 210 °C with an obvious weight loss step of 6% was exhibited within 100–220 °C on the DTA and TG curves, respectively. This may be corresponding to the loss of residual water and hydroxide in the raw materials. The second step of weight loss (4%) arising at 220–260 °C is due to the decomposition of carbonates, accompanied with an exothermic peak appearing at 240 °C on the DTA curve. From 260–350 °C, the third weight loss of 3% was found in the TG curve. At the same time, an exothermic DTA peak was observed at 320 °C, attributed to the decomposition of the decomposition ammonium vanadate. Above 350 °C, the TG and DTA curves almost unchanged, indicating that no obvious chemical reaction and phase transformation occur in the sample.

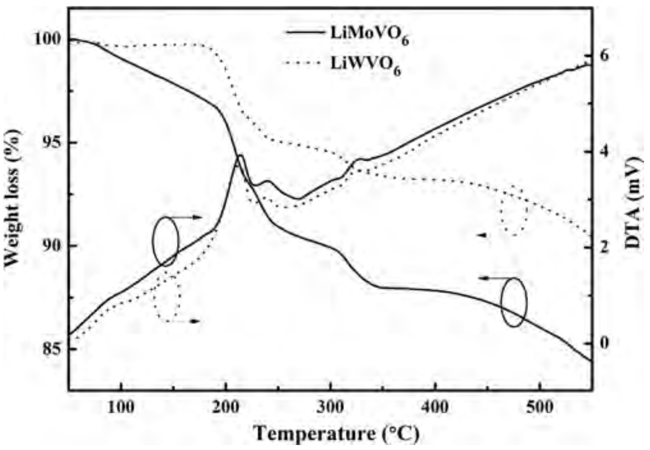

Fig 1. TG-DTA curves of the uncalcined mixed raw powders for $LiMVO_6$ (M = Mo, W).

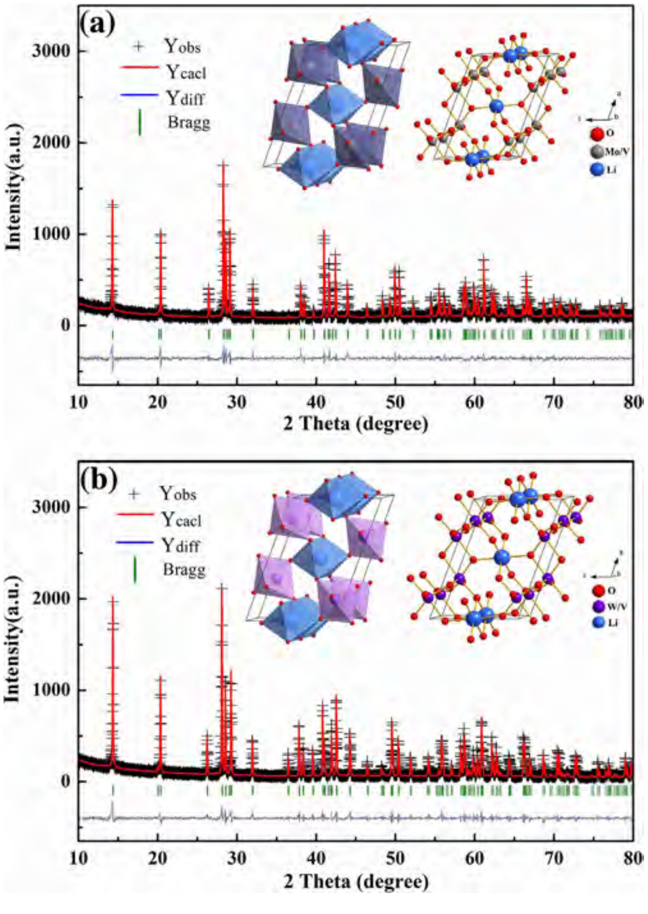

Fig. 2. Rietveld refinement patterns and crystal structure of (a) $LiMoVO_6$ and (b) $LiWVO_6$ samples calcined at 500 °C and 600 °C for 6 h, respectively.

Rietveld refinement patterns based on the XRD data of $LiMoVO_6$ and $LiWVO_6$ samples calcined at 500 °C and 600 °C for 6 h, respectively were displayed in Fig. 2. Both compounds crystallized in a monoclinic brannerite structure with a space group *C2/m*. The lattice parameters are $a = 9.3535(1)$ Å, $b = 3.6509(7)$ Å, $c = 6.6422(8)$ Å for $LiMoVO_6$ and $a = 9.3699(5)$ Å, $b = 3.6706(3)$ Å, $c = 6.6258(2)$ Å for $LiWVO_6$, respectively. The crystal structures are also illustrated in the inset of Fig. 2. It shows that both Li and M atoms locate in oxygen octahedral sites. The LiO_6 octahedra are edge-sharing while MO_6 are corner-shared octahedra. In addition, the LiO_6 octahedrons and MO_6 octahedrons are corner shared. In short, the $LiMVO_6$ structure

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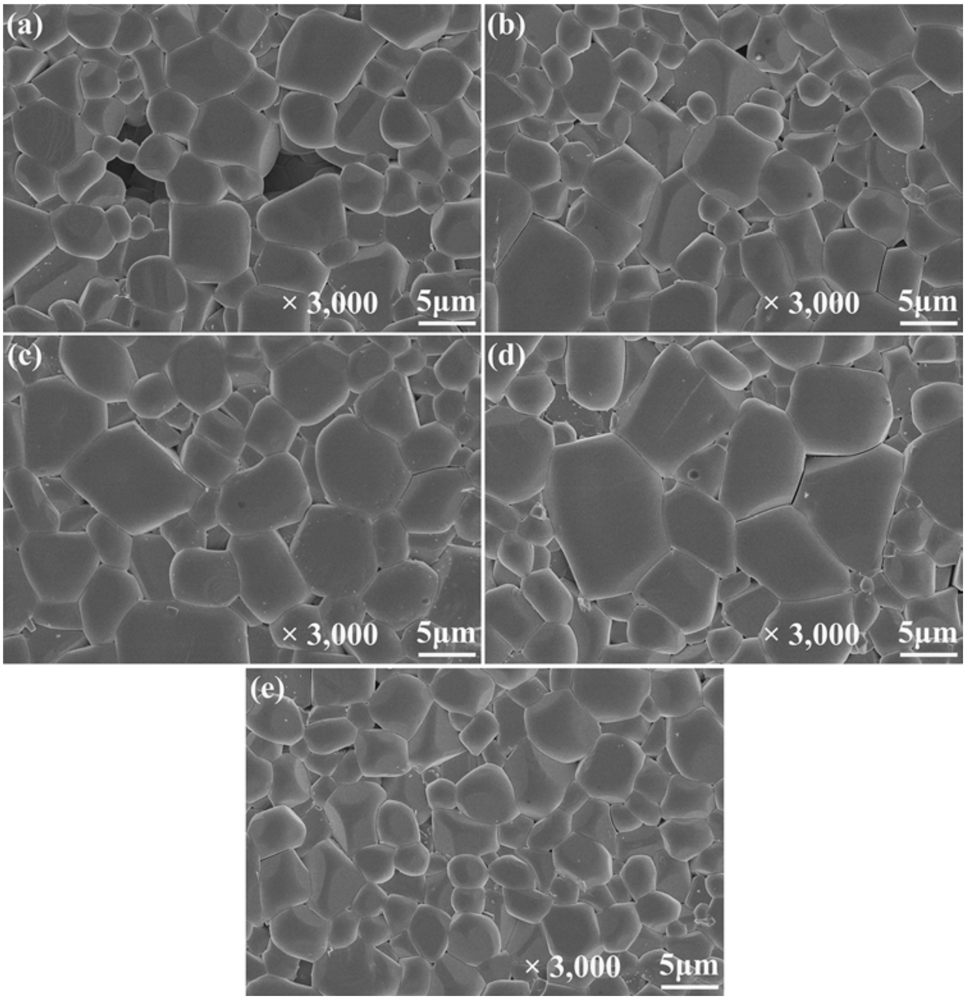

Fig. 3. FE-SEM images of polished and thermally etched of $LiWVO_6$ ceramic sintered at (a) 660 °C, (b) 680 °C, (c) 700 °C, (d) 720 °C, and $LiMoVO_6$ ceramic sintered at (e) 640 °C.

can be viewed as interconnected octahedra with shared oxygen atoms at the corners.

3.2. Microstructure characteristics

Fig. 3 shows SEM micrographs of polished and thermally etched of $LiMVO_6$ ceramics sintered at various temperatures, (a-d) for $LiWVO_6$ and (e) for its Mo counterpart. When sintered at low temperatures, porous microstructures were developed. For example, some pores existed in the $LiWVO_6$ ceramic sintered at 660 °C as shown in Fig. 3(a). With increasing sintering temperature, the amount of pores gradually decreased and uniform and dense microstructures with closely packed grains were obtained at optimum sintering temperature 700 °C for $LiWVO_6$. A further increase in the sintering temperature of $LiWVO_6$ to 720 °C leads to an over-sintering, resulting in abnormal grain growth with large grains (~10 μm) and some porosity in the sample. Similarly, a similar microstructure evolution in the $LiMoVO_6$ ceramics to the $LiWVO_6$ is observed, and the sample sintered at 640 °C exhibited a relatively dense microstructure, as shown in Fig. 3(e). However, when the sintering temperature increased to 650 °C, the partial grain melting was observed in $LiMoVO_6$ ceramic. This result is consistent with the previous report that the decomposition temperature of $LiMoVO_6$ is 650 °C [17,18].

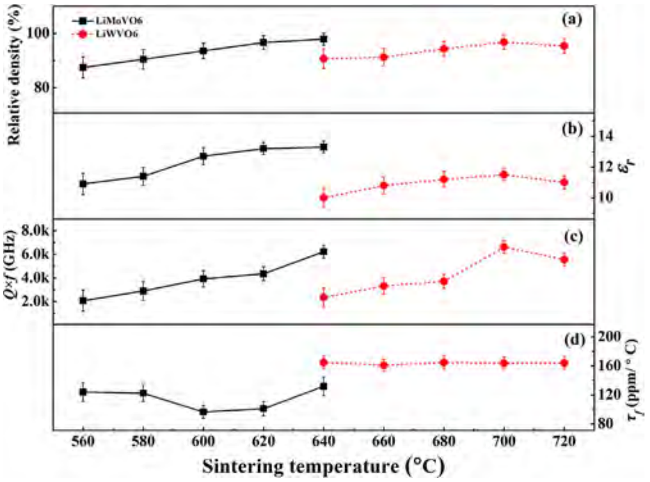

Fig. 4. The variation of relative density and microwave dielectric properties (ε_r, $Q\times f$, and τ_f) of $LiMVO_6$ (M = Mo, W) ceramics as a function of sintering temperature.

3.3. Microwave dielectric properties

Fig. 4 shows the variations in the relative density, ε_r, $Q\times f$, and τ_f of $LiMVO_6$ (M = Mo, W) ceramics as a function of sintering temperature. As the sintering temperatures increased from 560 °C to 640 °C, the relative density of $LiMoVO_6$ ceramic gradually increased from

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87.5% to 97.9% of the theoretical density (~3.93 g/cm^3). For $LiWVO_6$ ceramics, the variation in relative density with increasing sintering temperature exhibited a similar trend. A maximum value ~96.8% of the theoretical density 5.29 g/cm^3 was obtained at 700 °C. By comparison, the densification temperature and apparent density of $LiMoVO_6$ ceramic are much lower than its W counterpart.

As shown in Fig. 4(b), the relative permittivity of $LiMoVO_6$ ceramic increased from 10.9 to 13.3 with increasing sintering temperatures from 560 °C to 640 °C. For $LiWVO_6$ ceramics, in the sintering temperature range 640–720 °C, the ε_r firstly increased from 10.0 to 11.5, and then slightly decreased to 11.0. The ε_r exhibits similar variation tendency to the relative density, indicating that the density exerts critical effects on the relative permittivity.

Fig. 4(c) shows the quality factors of the $LiMVO_6$ (M = Mo, W) ceramics sintered at different temperatures. Similar to the variation in relative permittivity, $Q \times f$ value of $LiMoVO_6$ ceramic increased from 4156 GHz to 12,464 GHz with increasing sintering temperature. For $LiWVO_6$ ceramic, a maximum $Q \times f$ value of 13,264 GHz was obtained at 700 °C. The relationship between the packing fraction and the quality factor was proposed by Kim et al. [19]. The packing fraction could be defined as:

$$\text{packing fraction} \quad (\%)\frac{\text{volume of packed ions}}{\text{volume of unit cell}} \times Z \tag{1}$$

where, Z is the number of formula units per unit cell. The packing fraction of $LiMoVO_6$ is 67.2%, smaller than that of $LiWVO_6$ (~68.0%). Thus, the lower $Q \times f$ value of $LiMoVO_6$ than that of $LiWVO_6$ might be partly due to the smaller packing fraction. As shown in Fig. 4(d), the τ_f value exhibited weak dependence on sintering temperature with a value of +101.0 ppm/°C for $LiMoVO_6$ sintered at 640 °C and +163.8 ppm/°C for $LiWVO_6$ ceramic sintered at 700 °C for 6 h.

Table 1 shows the M-site bond valence for $LiMVO_6$ (M = Mo, W) ceramics, calculated using the following equations [20]:

$$V_i = \sum_j vij \tag{2}$$

$$V_{ij} = \exp\left[\frac{Rij - dij}{b}\right] \tag{3}$$

where R_{ij} is the bond valence parameter, d_{ij} is the length of a bond between atoms i and j, and b is a universal constant (0.37 Å) [21]. It is obvious that as the M-site bond valence decreased, the τ_f values of $LiMVO_6$ (M = Mo, W) ceramics increased. According to the bond valence theory, the shorter the bond length is, the stronger the bond energy become. The atomic interaction results in the changes to the bond valences of the materials [22,23]. The relationship between bond valence and the temperature coefficient of resonant frequency could be attributed to the tilting of oxygen polyhedra with the bond valence [24,25]. Table 1 also lists the octahedral distortion (Δ) obtained from the following equation [26]:

$$\Delta = \frac{1}{6}\sum\left\{\frac{R_i - \bar{R}}{R}\right\}^2 \tag{4}$$

where R_i is the individual bond length and R is the average bond length of the oxygen octahedron. With a decrease in octahedral distortion, theτ_f value increased. Similar reports were also found in $Ba(Co_{1\text{-}x}Mg_x)_2(VO_4)_2$ [23], $NdNbO_4$ [24], and $AZrNb_2O_8$ [27] systems. The average bond strength could decrease with decreasing M-site bond valence, resulting in the decreasing restoring force for recovering the tilting of octahedra, and τ_f value would thereupon increased.

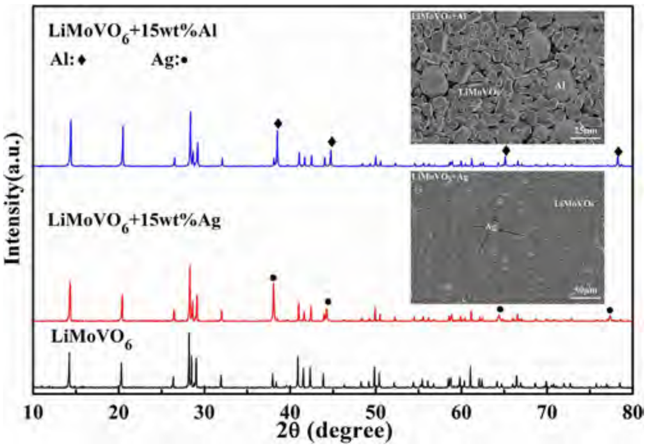

Fig. 5. XRD patterns and SEM images of $LiMoVO_6$ ceramic sintered at 640 °C for 6 h, and the sample cofired with 15 wt.% Al and 15 wt.% Ag at 640 °C for 6 h.

Table 2 lists the sintering temperature, the microwave dielectric properties and chemical compatibility with metal electrodes of some ultra-low temperature-firing ceramics. The sintering temperatures of the $LiMVO_6$ (M = Mo, W) ceramics are compatible with the other molybdates and vanadates. Moreover, it is found that most of the Mo-containing microwave dielectric ceramics possess large negative τ_f values, which would limit their commercial applications [28]. Thus, the large positive τ_f values of $LiMVO_6$ (M = Mo, W) make them promising τ_f compensators to adjust the temperature stability of some molybdates.

3.4. Chemical compatibility with metal electrodes

The chemical compatibility with metal electrodes was investigated by co-firing the $LiMoVO_6$ powders with pure aluminum and silver powders (15 wt.%) at 640 °C for 6 h in air. shows the XRD patterns of the co-fired samples with aluminum and silver and that of the pure $LiMoVO_6$ ceramic is also presented for comparison. XRD analysis (as shown in Fig. 5) reveals that only the diffraction peaks of $LiMoVO_6$ and metal electrodes could be detected, suggesting no reaction between them. SEM images (as shown in the inset of Fig. 5) of the cofired ceramics exhibited distinct difference in grain morphology and element contrast between the matrix and electrodes, further confirming their chemical compatibility. However, for $LiWVO_6$ sample, chemical reaction between $LiWVO_6$ with silver to form LiAgO and $AgV_2O_{5.5}$ was observed.

4. Conclusions

Two novel low-firing microwave dielectric ceramics, $LiMVO_6$ (M = Mo, W), were prepared. Both ceramics crystallized into a brannerite structure with a space group *C2/m* and could be well densified at temperature lower than 700 °C with relative densities larger than 95%. The microwave dielectric properties were characterized with low relative permittivity of 11–14, moderate quality factors 12,460–13,260 GHz, and relatively large positive τ_f of 101.0–163.8 ppm/°C. The relationship between the microwave dielectric properties and crystal structure were evaluated based on the packing fraction, bond valence, and oxygen octahedral distortion. Moreover, $LiMoVO_6$ ceramic was found to be chemically compatible with aluminum and sliver and the $LiWVO_6$ ceramic could be chemically compatible with aluminum. These results indicate that $LiMVO_6$ (M = Mo, W) ceramics are potential candidates for LTCC applications.

Acknowledgments

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Table 1
Bond valence and octahedral distortion of LiMVO$_6$ (M = Mo, W) ceramics.

M	R_A (Å)	R_M (Å)	$d_{M\text{-}O1}$ (Å)	$d_{M\text{-}O2}$ (Å)	$d_{M\text{-}O3}$ (Å)	$d_{A\text{-}O1}$ (Å)	$d_{A\text{-}O2}$ (Å)	$d_{A\text{-}O3}$ (Å)	V_A	V_M	V_O	Octahedral distortion ($\Delta 10^{-3}$)
Mo	1.466	1.907	1.728	1.921	1.874	2.167	2.167	2.304	0.717	6.830	2.270	17.1
W.	1.466	1.921	1.905	1.599	1.758	2.468	2.468	1.998	0.760	6.332	2.380	3.5

Table 2
Microwave dielectric properties of some low-temperature cofired ceramics.

Ceramics	S.T. (°C)	ε_r	Q × f (GHz)	τ_f (ppm/°C)	Reactivity with Ag or Al	Reference
Na$_2$MoO$_4$	660	4.1	35,000	−76	no with Ag and Al	[29]
Li$_2$MoO$_4$.	540	5.5	46,000	−160	yes for Ag, no for Al	[30]
Li$_2$WO$_4$	640	5.5	62,000	−146	yes for Ag, no for Al	[31]
K$_2$Mo$_3$O$_{10}$	520	5.6	35,800	−92	yes for Ag, no for Al	[32]
K$_2$Mo$_4$O$_{13}$	540	6.8	39,800	−67	yes for Ag, no for Al	[33]
K$_2$Mo$_2$O$_7$	460	7.5	22,300	−63	yes for Ag, no for Al	[33]
Li$_2$Ca$_2$Mo$_3$O$_{12}$	630	8.5	108,000	−89	no with Ag and Al	[34]
Li$_3$AlMo$_3$O$_{12}$	570	9.5	50,000	−73	no with Ag and Al	[35]
BaV$_2$O$_6$	550	11.2	42,800	+28	no with Al	[36]
LiWVO$_6$	700	11.5	13,260	+163.8	yes for Ag, no for Al	This work
LiMoVO$_6$	640	13.3	12,460	+101.0	no with Ag and Al	This work

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